

A Study of the Transference Numbers of
Sulfuric Acid and the Influence of
Gelatin on the Transference
Numbers by the Concen-
tration Cell Method

A THESIS

SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE
UNIVERSITY OF MICHIGAN IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY
June 1921

By

Wesley George France

EASTON, PA.
ESCHENBACH PRINTING COMPANY
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A STUDY OF THE TRANSFERENCE NUMBERS OF SULFURIC ACID AND THE INFLUENCE OF GELATIN ON THE TRANSFERENCE NUMBERS BY THE CONCENTRATION CELL METHOD

INTRODUCTION.

Three methods have been used for the determination of transference numbers; the analytical, the moving boundary, and the concentration cell. The oldest and most generally used is the analytical discovered by W. Hittorf. The moving boundary method was first described by O. Lodge and has been developed and used by R. B. Dension and B. D. Steele. The concentration cell method has been used in only a few cases and with varying success; its reliability for uni-univalent electrolytes, however, has been demonstrated in this laboratory.

The present investigation is an application of the concentration cell method to the determination of the transference numbers of a uni-bivalent electrolyte. In the first part of the work the electrolyte used was sulfuric acid, and in the second part sulfuric acid plus definite quantities of gelatin.

Historical.¹

The first investigator to develop a successful method for the determination of transference numbers was W. Hittorf. (*Pogg. Ann.*, **89**, 177 (1853)). In this work an electrolytic cell was used in which a strip of silver always served as cathode and a metal which corresponded to the metal ion of the electrolyte as anode. The transference numbers were calculated from the change in concentration around the anode which resulted from the passage of a measured quantity of electricity. This method was improved in many respects by him during the next few years and, as finally used, was the same in all essentials as the present Hittorf method.

Hittorf is given credit for the origination of this method for the determination of transference numbers, although there were several earlier investigations on the changes which take place about the electrodes during electrolysis. As early as 1814 R. Porrett (*Abst. Phil. Trans.*, **1**, 510) investigated the movement of iron and potassium ions when a solution of ferrocyanic acid was electrolyzed. M. Faraday (*Phil. Trans.* **123**, 682, 525, (1833)) studied the relative changes in acidity produced by electrolysis in equivalent solutions of NaOH and H₂SO₄. J. F. Daniell (*Phil. Trans.*, **129**, 97 (1839); **130**, 209 (1840)); J. F. Daniell and W. A. Miller (*ibid.*, **134**, 1 (1844)); and M. Pouillet (*Comptes rendus*, **20**, 1 sem. 1544 (1845)) conducted similar investigations and were able to calculate from their

¹ For a complete abstract and bibliography of Transference Numbers up to and including the work of 1905, see J. W. MacBain. (*J. Wash. Acad. Sci.*, **9**, 1.)

results migration ratios. The values so obtained are approximations only, since strict quantitative procedures were not employed.

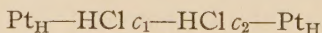
The moving boundary or direct method for the measurement of the migration velocity of ions was first described by O. Lodge (*Brit. Assoc. Rep.*, 389 (1886)). Two cups with suitable electrodes and electrolytes were connected by means of a horizontal siphon filled with gelatin which contained phenolphthalein or some salt. When a current was passed through the apparatus the diffusion of the ions caused either a color change or a precipitation in the gelatin. As the diffusion progressed the color change or precipitation produced a sharp boundary. From the velocity of movement of this boundary the transference numbers were calculated.

The concentration cell method was first suggested by von Helmholtz (*Ges. Abh.*, I 840, II 979). By the use of thermodynamic principles together with the phenomenon of vapor pressure, he showed that transference numbers can be expressed by the ratio of the potential of a concentration cell with diffusion to that of a concentration cell without diffusion. This method appears open to fewer objections than either the analytical or moving boundary methods. It has, however, been used less extensively than the others. This is undoubtedly due to the difficulties encountered in the construction of suitable electrodes.

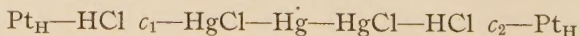
The method was first experimentally tested by J. Moser (*Wien. Sitzungsber.*, 92, *Abth.* II, 652 (1885)). He obtained for the transference numbers of the anions of ZnSO_4 and ZnCl_2 .64 and .71 which agreed well with the values, .636 and .700, obtained by Hittorf.

No further use of the method was made until 1898. At this time G. Kümmell (*Wied. Ann.*, 64, 655) determined the transference numbers of ZnCl_2 , ZnSO_4 , CdCl_2 , and CdSO_4 . These results did not agree well with those obtained by Hittorf.

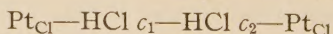
The same year D. McIntosh (*J. Phys. Chem.*, 2, 273) made an investigation of the method. The transference number of the hydrogen ion in H_2SO_4 , HCl , HBr , HI , and $\text{H}_2\text{C}_2\text{O}_4$ was determined. In most of the work cells of the types



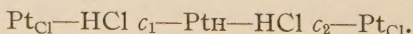
and



were used. However some work was done with cells of the types



and



As a result of his investigation, McIntosh was led to conclude that the method was not suitable for use with gas cells. This conclusion appears to be founded on two facts; the failure of the cells of the first type to give

values in agreement with those of the second, and the lack of agreement between the velocity which he obtained for the hydrogen ion and that calculated from the conductivity data of Kohlrausch. That this conclusion was not entirely justified is evident from a consideration of the rather wide variation between the cells intended to be duplicates. The variation in some cases is .0015 volt. There also appears to have been no effort made to maintain the cells at a constant temperature. From the results obtained later, by other investigators, it appears that his difficulty was not inherent in the method, but in the construction of the electrodes.

The same method was employed by D. A. MacInness and K. Parker in their determination of the transference numbers of KCl (*J. A. C. S.*, **37**, 1445 (1915)). They used potassium amalgam and silver chloride electrodes and obtained satisfactory results.

The most recent application of the method was in the investigation of the transference numbers of HCl by A. L. Ferguson (*J. Phys. Chem.*, **20**, 326 (1916)). Hydrogen and calomel electrodes were used the temperature was maintained at 25° C. The potentials were measured to .00001 volt and the maximum variation of the cells was about .0001 volt. The transference numbers obtained agreed very well among themselves and also with the best accepted values of other investigators. This work resulted in the establishment of the value and reliability of the method when hydrogen gas cells are used. This is in direct contradiction to the conclusion arrived at by MacIntosh eighteen years earlier.

There is no accurate work, thus far, on the application of the method to uni-bivalent electrolytes.

Theoretical

The determination involves the measurement of the potentials of a concentration cell without diffusion; a concentration cell with diffusion and reversible with respect to the cation; and a concentration cell with diffusion and reversible with respect to the anion.

The total potential of the concentration cell, reversible with respect to the cation, $\text{Pt}_H | \text{H}_2\text{SO}_4 \ c_1 | \text{H}_2\text{SO}_4 \ c_2 | \text{Pt}_H$, consists of the algebraic sum of the two electrode potentials and the potential at the boundary of the solutions. On the assumption that sulfuric acid dissociates into two hydrogen ions and one sulfate ion, the algebraic sum of the electrode potentials is expressed by the well-known formula

$$E_1 = \frac{RT}{F} \ln \frac{c_1}{c_2} \quad (1)$$

The potential at the liquid boundary is expressed by the formula

$$E_B = \frac{2U_c - U_a}{2(U_c + U_a)} \frac{RT}{F} \ln \frac{c_1}{c_2} \quad (2)$$

The hydrogen electrode in the concentrated solution is positive with respect to the hydrogen electrode in the dilute solution. At the boundary of the solutions, the sulfuric acid diffuses from the concentrated to the dilute side, and since the hydrogen ion moves faster than the sulfate ion, the dilute side is positively charged with respect to the concentrated. This means that the potential developed at the boundary opposes the potential of the hydrogen electrodes. The total potential of the hydrogen concentration cell is, therefore, expressed by the equation

$$E_1 - E_B = E_s = \frac{RT}{F} \ln \frac{c_1}{c_2} - \frac{2U_c - U_a}{2(U_c + U_a)} \frac{RT}{F} \ln \frac{c_1}{c_2}$$

$$= \left[1 - \frac{2U_c - U_a}{2(U_c + U_a)} \right] \frac{RT}{F} \ln \frac{c_1}{c_2} = \frac{3}{2} \frac{U_a}{U_c + U_a} \frac{RT}{F} \ln \frac{c_1}{c_2}$$

By the substitution of the transference number of N_a , of the anion for $U_a/(U_a + U_c)$ the equation

$$E_H = \frac{3}{2} N_a \frac{RT}{F} \ln \frac{c_1}{c_2} \quad (3)$$

is obtained.

The total potential of the concentration cell, reversible with respect to the anion $\text{Hg} \mid \text{Hg}_2\text{SO}_4, \text{H}_2\text{SO}_{4C_1} \mid \text{H}_2\text{SO}_{4C_2}, \text{Hg}_2\text{SO}_4 \mid \text{Hg}$, consists of the algebraic sum of the two electrode potentials and the potential at the boundary of the solutions. The algebraic sum of the electrode potentials is expressed by the formula

$$E_4 = \frac{RT}{2F} \ln \frac{c_1}{c_2} \quad (4)$$

The boundary potential is the same as in the hydrogen concentration cell, and is in the same direction. The algebraic sum of the sulfate electrode potentials is also in this direction. Therefore the total potential of the sulfate concentration cell is expressed by the equation

$$E_4 + E_B = E_{\text{SO}_4} = \frac{RT}{2F} \ln \frac{c_1}{c_2} + \frac{2U_c - U_a}{2(U_c + U_a)} \frac{RT}{F} \ln \frac{c_1}{c_2}$$

$$= \left[\frac{1}{2} + \frac{2U_c - U_a}{2(U_c + U_a)} \right] \frac{RT}{F} \ln \frac{c_1}{c_2} = \frac{3}{2} \frac{U_c}{U_c + U_a} \frac{RT}{F} \ln \frac{c_1}{c_2}$$

By the substitution of the transference number, N_c , of the cation for the expression $U_c/(U_a + U_c)$ the equation becomes

$$E_{\text{SO}_4} = \frac{3}{2} N_c \frac{RT}{F} \ln \frac{c_1}{c_2} \quad (5)$$

The potential of the concentration cell without diffusion, $\text{Pt}_H \mid 0.1 M \text{H}_2\text{SO}_4, \text{Hg}_2\text{SO}_4 \mid \text{Hg} \mid \text{Hg}_2\text{SO}_4, 0.01 M \text{H}_2\text{SO}_4 \mid \text{Pt}_H$, is represented by the equation

$$E = \frac{3}{2} \frac{RT}{F} \ln \frac{c_1}{c_2} \quad (6)$$

The value E may be obtained experimentally from the difference between the potentials of the cells $\text{Pt}_\text{H} | 0.1 \text{ M } \text{H}_2\text{SO}_4, \text{Hg}_2\text{SO}_4 | \text{Hg}$, and $\text{Pt}_\text{H} | 0.01 \text{ M } \text{H}_2\text{SO}_4, \text{Hg}_2\text{SO}_4 | \text{Hg}$.

Equation 5 divided by Equation 6 gives $E_{\text{SO}_4}/E = N_c$, which expresses the transference number of the cation in terms of E_{SO_4} and E . In a similar way the expression $E_\text{H}/E = N_a$, is obtained, as $N_a + N_c = 1$, therefore $E_{\text{SO}_4}/E + E_\text{H}/E = 1$; and

$$E_{\text{SO}_4} + E_\text{H} = E. \quad (7)$$

It is evident from Equation 7 that the same value should be obtained by the sum of the potentials E_{SO_4} and E_H as by the difference of the potentials $E_{0.01}$ and $E_{0.1}$.

Since, to obtain the total potential, E_{SO_4} , the boundary potential is added to the electrode potentials, while for the total potential, E_H , it is subtracted, then, by a combination of these as shown below, a formula is obtained which expresses the boundary potential in terms of E_{SO_4} and E_H .

$$\begin{aligned} E_\text{H} &= \frac{RT}{F} \ln \frac{c_1}{c_2} - \frac{(2-3N_a)RT}{2} \ln \frac{c_1}{c_2}; E_{\text{SO}_4} = \frac{RT}{2F} \ln \frac{c_1}{c_2} + \frac{(2-3N_a)RT}{2} \ln \frac{c_1}{c_2}; \\ 2E_{\text{SO}_4} &= \frac{RT}{F} \ln \frac{c_1}{c_2} + \frac{2(2-3N_a)RT}{2} \ln \frac{c_1}{c_2} \\ \frac{2E_{\text{SO}_4} - E_\text{H}}{3} &= \frac{(2-3N_a)RT}{2} \ln \frac{c_1}{c_2}. \end{aligned} \quad (8)$$

Therefore the value for the boundary potential may be obtained by the substitution of the measured potentials E_{SO_4} and E_H in the above equation.

Apparatus and Materials.

The potential measurements were made with an Otto Wolff 15,000-ohm potentiometer, using a certified Weston cell as a standard. The solutions were prepared from a commercial c. p. sulfuric acid of 1.84 sp. gr. and were standardized by means of sodium carbonate prepared by the fusion of c. p. sodium hydrogen carbonate in an atmosphere of carbon dioxide. The mercurous sulfate was electrolytically prepared by the Hulett² method. The hydrogen was obtained by the electrolysis of 5 *N* sodium hydroxide solution using a generator similar to that of Bodenstein and Pohl,³ and the hydrogen electrodes were of the ordinary foil type. The mercury used was twice distilled. All measurements were made with the cells contained in an electrically heated and regulated oil thermostat maintained at a constant temperature of 25°.

The concentration cell method, as previously shown, requires the consecutive measurement of 4 distinct potentials which must be extremely constant and reproducible. Much experimental work was required before the satisfactory system of cells shown in Fig. 1 was developed. In this

² Hulett, *Phys. Rev.*, **32**, 257 (1911).

³ Bodenstein and Pohl, *Z. Elektrochem.*, **11**, 373 (1905).

arrangement the connections, between the separate cells, are made by means of siphons (M, N, H and G). A method whereby they could be filled with the proper solutions before being connected with the arms of the containers was considered essential. In this way new boundaries could be introduced without disturbing the electrodes. Connections were made with the cells through the reservoirs (R_a , R_b , R_c , R_d , Fig. 1) on the arms of the containers.

Arrangement of Cells and Method of Procedure.

In Fig. 1, A and B are the mercurous sulfate electrodes; C and D are the hydrogen electrodes. A and C contain 0.1 *M* and B and D 0.01 *M* sulfuric acid. The electrodes A and C are connected by the siphon H, B and D by the siphon G. The two sulfate electrodes are connected by the siphon M; the two hydrogen electrodes by the siphon N.

The containers were fastened in their proper position and filled with the electrode materials. The siphons H and G were put in place and filled by suction. The stopcocks J and O, P and K were then closed. The hydrogen was admitted to C and D through the inlets S and S' and bubbled through the solutions. It escaped through the outlets W and W' into

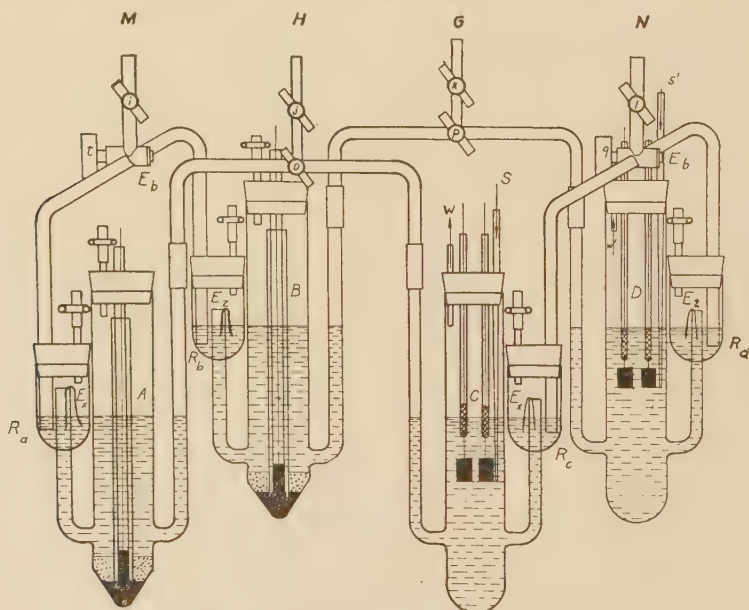


Fig. 1.—Arrangement of cells as used.

chambers (not shown) of about 10 cc. capacity. When the hydrogen electrodes became constant, the stopcock O was opened long enough to measure the potential $E_{0.1}$ between the sulfate and hydrogen electrodes in 0.1 *M* sulfuric acid solution. In a similar way the measurement $E_{0.01}$

was made for the sulfate and hydrogen electrodes in 0.01 *M* sulfuric acid. By the proper manipulation of the stopcocks, the solutions in those halves of siphons H and G connected to the sulfate electrodes were emptied. The arms of the siphons M and N with the rubber stoppers attached were immersed in 2 beakers which contained 0.1 *M* and 0.01 *M* sulfuric acid. The solutions were drawn into the arms of the siphons and formed the boundary within the stopcocks t and q. These siphons were then placed in their proper positions connecting the cells.⁴ The stopcock q was opened and the potential E_H of the hydrogen concentration cell measured. In a similar way the potential of the sulfate concentration cell (E_{SO_4}) was measured.

The leads from the electrodes were permanently connected to a switch-board so the potentials between any two electrodes could be measured by the manipulation of a switch connected to the potentiometer.

In the first part of the work the measurements showed considerable fluctuation, which was traced to the leakage of current from the high potential electrical circuits in connection with the thermostat. The difficulty was overcome by the replacement of the water by kerosene.

During the development of this work some information was obtained which may be of assistance to others concerned with similar investigations. It was found that the length of time required for the mercurous sulfate electrodes to reach a condition of equilibrium could be greatly reduced by vigorously shaking the sulfuric acid and mercurous sulfate in a mechanical shaker before using in the cells. The first cells constructed contained the hydrogen electrodes in the same chamber as the mercurous sulfate electrode and the potentials were found to vary greatly. This was believed to be due to the catalytic effect of the platinum black which was loosened by the action of the hydrogen on the electrode and fell on to the mercurous sulfate. The difficulty was eliminated by the use of separate chambers for the electrodes.

Experimental Results with Sulfuric Acid.

The final measurements were made and are given in four tables of which I and II are examples.

In these tables Col. E_H contains the potentials of the hydrogen concentration cell with diffusion, $Pt_H | 0.1 M H_2SO_4 | 0.01 M H_2SO_4 | Pt_H$; Col. E_{SO_4} those of the sulfate concentration cell with diffusion, $Hg | Hg_2SO_4 | 0.01 M H_2SO_4 | 0.1 M H_2SO_4, Hg_2SO_4 | Hg$; Col. $E_{0.1}$ the potentials of the cell $Pt_H | 0.1 M H_2SO_4, Hg_2SO_4 | Hg$; and Col. $E_{0.01}$ the potentials of the cell, $Pt_H | 0.01 M H_2SO_4, Hg_2SO_4 | Hg$. The column headed " E by $E_H + E_{SO_4}$ " contains the sums of the values recorded in Cols. E_H

⁴ In the measurement for the transference numbers of H_2SO_4 the reservoirs (R_a, R_b, R_c, R_d) were filled above the openings of the side arms. In the later work when gelatin was used they were filled as shown in the diagram.

TABLE I.

No.	Date.	Time.	Bar. Mm.	E_H	E_{SO_4}	$E_{0.1}$	$E_{0.01}$	E by $E_H + E_{SO_4}$	E by $E_{0.01} - E_{0.1}$
1	10/13	3:00 P.M.	741.6			0.74202	0.80260		
2	10/13	4:00	741.6			0.74200	0.80260		
3	10/13	7:30	740.4	0.01137	0.04933	0.74205	0.80275	0.06070	0.06070
4	10/13	9:00	740.0	0.01139	0.04930	0.74210	0.80274	0.06069	0.06064
5	10/13	10:30	740.0	0.01139	0.04929	0.74212	0.80276	0.06068	0.06064
6	10/13	11:30	739.5	0.01141	0.04928	0.74212	0.80279	0.06069	0.06067
7	10/14	10:00 A.M.	736.0	0.01136	0.04900	0.74203	0.80249	0.06036	0.06036
8	10/14	1:30 P.M.	734.5	0.01133	0.04913	0.74201	0.80246	0.06046	0.06035
9	10/14	3:30	734.5	0.01130	0.04918	0.74203	0.80245	0.06048	0.06042
		Av.		0.01136	0.04922	0.74207	0.80263	0.06058	0.06056

The cell was set up at 9:00 A.M. on October 13, 1919.

TABLE II.

1	10/15	10:00 A.M.	739.3			0.74166	0.80192		
2	10/15	1:30 P.M.				0.74209	0.80263		
3	10/15	5:45				0.74200	0.80268		
4	10/15	7:15				0.74205	0.80269		
5	10/15	10:00	737.3	0.01136	0.04922	0.74195	0.80256	0.06058	0.06061
6	10/15	12:00	737.0	0.01127	0.04921	0.74212	0.80257	0.06048	0.06045
7	10/16	9:00 A.M.	736.3	0.01120	0.04927	0.74209	0.80253	0.06047	0.06044
8	10/16	10:30	736.5	0.01121	0.04923	0.74210	0.80247	0.06044	0.06037
		Av.		0.01126	0.04923	0.74206	0.80253	0.06049	0.06047

The cell was set up at 11 P.M. on October 14, 1919.

and E_{SO_4} . The column " E by $E_{0.01} - E_{0.1}$ " contains the differences between the values recorded in $E_{0.01}$ and $E_{0.1}$.

The 0.1 M and 0.01 M cells were prepared and placed in the thermostat where they remained for about 12 hours to come to equilibrium before the boundaries were introduced. This accounts for the blank spaces in the tables.

As pointed out in the theoretical discussion the values recorded in column $E_H + E_{SO_4}$ should be equal to those recorded in column $E_{0.01} - E_{0.1}$. The close agreement of these values indicates the accuracy of the potential measurements. The differences between the successive values in each column indicates the degree of constancy of the cells. The differences in columns $E_{0.01}$ and $E_{0.1}$ may be attributed, in part, to changes in barometric pressure, for which corrections have not been applied, as such corrections are unnecessary for the calculations in which the measurements are used.

The remarkable agreement between the averages in the different tables indicates the reproducibility of the work.

In the theoretical treatment formulas were given by means of which the values of E , E_H , E_{SO_4} and E_B can be calculated. Table III contains a summary of such calculated values together with the measured values.

TABLE III.—COMPARISON BETWEEN CALCULATED AND MEASURED POTENTIALS.

		E' .	E'' .	E .	E_H .	E_{SO_4} .	E_B .
Calc. from	Cond.	0.10511	0.06693	0.08883	0.014716	0.06407	0.03781
	Fz. Pt.	0.08072		0.06054	0.011301	0.04918	0.02908
Measured				0.06054	0.011310	0.04925	0.02906

These calculations involve the ratio $\alpha_1 C_1 / \alpha_2 C_2$. It has been customary to use conductivity values in its calculation. Since the work of Jones is probably the most reliable on the conductivity of sulfuric acid, his results were used in these calculations. This ratio may also be obtained from freezing-point data. The values obtained from these two sources are decidedly at variance. No freezing-point data are available for the degree of dissociation of 0.1 *M* sulfuric acid. However, a complete table is given by Lewis and Linhart⁵ for concentrations between 10^{-2} and 10^{-6} molar. The degree of dissociation given by Lewis and Linhart for 0.01 *M* sulfuric acid was substituted in the equation for E together with the measured potential (0.06054), and the equation solved for the degree of dissociation for 0.1 *M* sulfuric acid. In the curve of Fig. 2 the abscissas are the molar concentrations and the ordinates the degrees

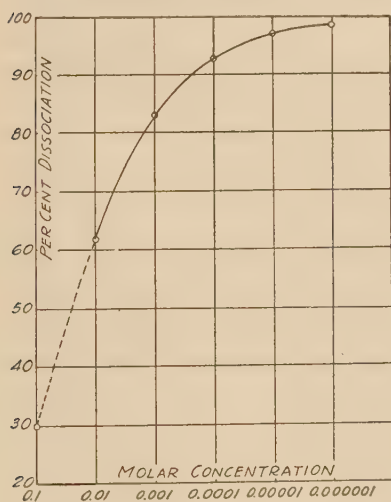


Fig. 2.—Dissociation-concentration curve.

of dissociation. The portion indicated by the solid line was obtained from the freezing-point data and the broken portion is an extension to include the value calculated from the potential measurements. Since this is a smooth curve, the indication is that the point obtained from the potential measurements is approximately the same as would have been obtained from the freezing-point determination. In every instance the results obtained when the freezing-point values are used in the ratio $\alpha_1 C_1 / \alpha_2 C_2$ show better agreement with the measured potentials than when the conductivity values are used. The latter results are in all cases higher than the measured. It should be noticed, however, that the exact agreement between the measured and calculated values for E is to be expected, since it was from this measured value of E that C_2 was calculated. The close agreement between the measured and calculated values of E_H , E_{SO_4} and E_B is a true indication of the correctness of the value 0.2973 for the degree of dissociation of 0.1 *M* sulfuric acid.

⁵ Lewis and Linhart, *J. Am. Chem. Soc.*, **41**, 1959 (1919).

It is important to note that all of the values thus far calculated are based on the assumption that sulfuric acid dissociates entirely into two hydrogen ions and one sulfate ion. Column E' shows the values for E calculated on the assumption that the sulfuric acid dissociates into one hydrogen ion and one hydrogen sulfate ion. The fact that the measured potentials agree so well with those calculated on the first assumption and do not agree with those calculated on the second assumption is a strong indication that the sulfuric acid dissociates almost entirely into 3 ions at these concentrations.

It has been noticed by others that the calculated values for potential measurements are always higher than the measured values when conductivity dissociation ratios are used. Ferguson⁶ in his work on hydrochloric acid attributed the difference to the fact that the formula assumes the complete dissociation of the acid. As the acid is not completely dissociated the formula does not exactly represent the facts and must be corrected so as to include the undissociated acid. Such a correction was made for hydrochloric acid and, when applied to the formulas involving conductivity ratios, gave values which agreed more closely with those measured. A similar correction can be developed for the sulfuric acid concentration cell.

When two faradays of electricity pass through a sulfuric acid concentration double cell, one mol of acid is transferred from one concentration to the other. The electrical work which accompanies this change is represented by $W = 2EF$. The osmotic work required to effect this same change is usually represented by $W = 3RT \ln c_1/c_2$. This assumes that the acid is completely dissociated into 3 ions. Since it is not completely dissociated what actually happens is (1) the transference of an amount of hydrogen ion equal to twice the concentration times the dissociation of the acid; (2) the transference of an amount of sulfate ion equal to the concentration times the dissociation of the acid; (3) the transference of an amount of undissociated acid equal to the concentration of the undissociated acid. The general expression which represents the sum of the osmotic work in (1) and (2) is $W_1 = \alpha 3RT \ln \frac{c_1}{c_2}$.

Similarly the osmotic work in (3) is $W = (1-\alpha)RT \ln \frac{c_1}{c_2}$. In the application to sulfuric acid (c_1) in (W_1) becomes $2c_1H^+ = 2c_1\alpha' = c_1SO_4^{--}$; and c_2 becomes $2c_2H^+ = 2c_2\alpha'' = c_2SO_4^{--}$.

Similarly c_1 in W_2 becomes $c_1H_2SO_4 = c_1(1-\alpha')$; and c_2 becomes $c_2H_2SO_4 = c_2(1-\alpha'')$; and, as the total electrical work is equal to the total osmotic work,

$$W = 2EF = \alpha 3RT \ln \frac{c_1\alpha'}{c_2\alpha''} + (1-\alpha)RT \ln \frac{c_1(1-\alpha')}{c_2(1-\alpha'')} \\ E = \alpha \frac{3RT}{2F} \ln \frac{c_1\alpha'}{c_2\alpha''} + \frac{(1-\alpha)RT}{2F} \ln \frac{c_1(1-\alpha')}{c_2(1-\alpha'')}.$$

⁶ *J. Phys. Chem.*, **20**, 326 (1916).

This formula cannot be taken as absolutely correct since it assumes that the dissociation is the same in both concentrations, which is not true.

The most reliable value that can be used for α is $\frac{\alpha' + \alpha''}{2}$, in which α' is the degree of dissociation in c_1 and α'' is the degree of dissociation in c_2 .

Col. E'' Table III shows the result of the application of this correction. It is evident that the correction is an improvement since the difference (0.00639) between the measured value and that calculated from the corrected formula is much less than the difference (0.01829) between the measured value and that calculated from the usual formula.

In the theoretical part of this work it was shown that the boundary potential can be calculated from the formula $E_B = \frac{2 - 3 N_c}{2} \frac{RT}{F} \ln \frac{c_1}{c_2}$;

also that $E_B = \frac{2E_{\text{SO}_4} - E_H}{3}$. Column E_B contains the results from the

calculation by the first formula. Again the close agreement between the measured and calculate values in the case of the freezing-point ratio and lack of agreement in the case of the conductivity ratio are evident.

MacInnes⁷ has developed a formula for boundary potentials of uni-univalent electrolytes which involves the transference number of the cation and the potentials of the cells with and without diffusion. He states that it "contains no assumption regarding the concentration of the ions of the solutions." In the following development the same reasoning is applied to the uni-bivalent acid, sulfuric acid, on the assumption that it dissociates into two hydrogen ions and one sulfate ion.

When two faradays of electricity pass through the cell the net result is the transference of one mol of sulfuric acid from the concentrated to the dilute side. The current is carried across the boundary between the two solutions by the transference of $2 N_c$ gram ions of hydrogen ions in one direction and $1 - N_c$ gram ions of sulfate ions in the opposite. The osmotic work at the boundary is proportional to the algebraic sum of the number of gram ions that have passed through it. Therefore the osmotic work W is proportional to $3N_c - 1$. The electrical work which accompanies the transference of one mol of sulfuric acid from the concentrated to the dilute side is equal to the product of the electromotive force of the cell and the number of faradays required to effect the transference. Since this is so, the following relation holds.

$$2EF:2E_B F::3:3N_c - 1$$

and $E_B = E(3N_c - 1)/3$; for E , $\frac{E_{\text{SO}_4}}{N_c}$ may be substituted since it has been

⁷ MacInnes, *J. Am. Chem. Soc.*, **37**, 2301 (1915).

shown that $N = \frac{E_{\text{SO}_4}}{E}$. The formula then becomes

$$E_B = E_{\text{SO}_4} (3N_c - 1) / 3N_c.$$

Substituting the correct values for N_c and E_{SO_4} , as measured, the value 0.02904 is obtained. This is in almost perfect agreement with the measured value 0.02906 and proves the validity of the formula.

That this expression $E_B = E_{\text{SO}_4} (3N_c - 1) / 3N_c$ is but another form of the usual expression $E_B = \frac{2-3N_a}{2} \frac{RT}{F} \ln \frac{c_1}{c_2}$ for boundary potential, can readily be shown, since

$$E_B = \frac{E_{\text{SO}_4}}{3N_c} (3N_c - 1) \quad (9)$$

and

$$E_{\text{SO}_4} = N_c \frac{3}{2} \frac{RT}{F} \ln \frac{c_1}{c_2}.$$

Substituting in (9)

$$E_B = \frac{N_c \frac{3}{2} \frac{RT}{F} \ln \frac{c_1}{c_2}}{3N_c} (3N_c - 1) = \frac{RT}{F} \ln \frac{c_1}{c_2} (3N_c - 1)$$

is obtained; as $(3N_c - 1) = (2 - 3N_a)$

$$E_B = \frac{RT}{F} \ln \frac{c_1}{c_2} (3N_c - 1) = \frac{2 - 3N_a}{2} \frac{RT}{F} \ln \frac{c_1}{c_2}.$$

Therefore

$$E_B = \frac{E_{\text{SO}_4}}{3N_c} (3N_c - 1) = \frac{2 - 3N_a}{2} \frac{RT}{F} \ln \frac{c_1}{c_2} = \frac{2E_{\text{SO}_4} - E_H}{3}.$$

A consideration of these formulas indicates the advantage of the formula $(2E_{\text{SO}_4} - E_H)/3$ since it contains no assumption regarding the concentration of the ions, nor does it require a knowledge of the transference numbers.

The averages of E_H , E_{SO_4} , and E from a few of the tables obtained are contained in Table IV, together with the transference numbers calculated from them.

TABLE IV.

SUMMARY OF POTENTIALS AND TRANSFERENCE NUMBERS.

Table.	E_H .	E_{SO_4} .	E or $E_{0.01} - E_{0.1}$.	N_a . E_H/E .	N_a . $1 - E_{\text{SO}_4}/E$.
II	0.01136	0.04922	0.06056	0.1875	0.1875
III	0.01126	0.04923	0.06047	0.1862	0.1862
IV	0.01137	0.04929	0.06059	0.1875	0.1874
V	0.01126	0.04927	0.06053	0.1868	0.1868
Av.	0.01131	0.04925	0.06054	0.1868	0.1868

To facilitate the comparison of the value obtained in this investigation with those obtained on others, a summary of such values is contained in Table V.

Attention should be called to the fact that the values recorded in columns E_H/E and $1-E_{SO_4}/E$ of Table IV are determined from separate and distinct potential measurements. The agreement between the successive values in each column and between the averages of the two columns demonstrates the reliability of the concentration cell method for the determination of the transference numbers of sulfuric acid.

TABLE V.
SUMMARY OF TRANSFERENCE NUMBERS OF SULFURIC ACID.

Investigator, ^a		Concentration.	Temp. °C.	N_a .	N_a corrected to 25°.
Bein	1898	0.24%	11	0.175±3	0.1804
McIntosh	1898	1.0–0.001 <i>M</i>	18	0.174±18	0.1817
Starck	1899	0.5–0.6%	17–20	0.145±7	
Jahn and Huybrechts	1902	0.06–0.005 <i>M</i>	18	0.176±4	0.1837
Eisenstein	1902	0.124 <i>M</i>	18	0.168±3	0.1757
Eisenstein	1902	0.01 <i>M</i>	30	0.188±1	0.1825
Tower	1904	0.1 <i>M</i>	20	0.1805	0.1860
Tower	1904	0.01 <i>M</i>	20	0.1809	0.1864
Whetham and Paine	1908	0.05 <i>M</i>	18	0.184	0.1917
France	1920	0.1–0.01 <i>M</i>	25	0.1868	0.1868

Experimental Results with Sulfuric Acid Containing Gelatin.

The properties of hydrophile colloids have been the subject of many investigations during the past few years. So far, no entirely satisfactory explanation has been offered for their action in the presence of electrolytes. The theories advanced are based largely on the measurements of osmotic pressure, conductivity, swelling and transference numbers.

There appear to be but three articles in the literature dealing with the influence of colloids on transference numbers and in each instance the analytical method was used.

Paul Richter⁹ investigated the influence of gelatin, gum arabic, agar-agar, and peptone on the transference number of the chloride ion of lithium, potassium and hydrogen chlorides.

A. Mutscheller¹⁰ investigated the influence of gelatin on the transference numbers of silver nitrate, cupric sulfate and zinc sulfate solution which contained definite quantities of a 1% gelatin solution.

According to his results the transference numbers of the nitrate and

^a The values and the limits of accuracy of the first six investigations are taken from MacBain's abstract of transference data (*J. Wash. Acad. Sci.*, 9, 11 (1905)). In the first six investigations the analytical method was employed. According to MacBain the results of Jahn and Huybrechts and of Tower are probably the most reliable. Whetham and Paine employed the conductivity method. The values in the last column were obtained from the values in the preceding column by the application of the temperature coefficients given by Tower (*J. Am. Chem. Soc.*, 26, 1038 (1904)).

⁹ Richter, *Z. physik. Chem.*, 80, 449 (1912).

¹⁰ Mutscheller, *Met. Chem. Eng.*, 13, 353 (1915); *J. Am. Chem. Soc.*, 42, 442 (1920).

sulfate ions decrease with an increase in the quantity of gelatin solution added. By the addition of sufficient quantities of gelatin solution, even negative values were obtained. He states that when the transference number of the anion is zero the conditions are most favorable for the deposition of the metal. The effect of the gelatin is accounted for on the assumption that it is positively charged and forms an "absorption compound" with the anions. This results in the partial or complete neutralization or even reversal of the original charge on the ions. The results obtained by Mutscheller for the sulfate and nitrate ions show effects of gelatin far in excess of those observed by Richter for the chloride ion.

It is well to emphasize here that the results obtained by Mutscheller, if correct, are indeed remarkable, but it is the opinion of the author that an error has been made in the calculations or in the recorded data. This subject is under investigation at the present time.

Mutscheller¹⁰ explains the effect of gelatin on the transference numbers of silver nitrate, cupric sulfate and zinc sulfate by the assumption that gelatin is positively charged and "absorbs" the negative ions. This causes a decrease in their velocity. According to Nernst the potential at the boundary of two solutions of different concentration depends upon the difference in velocities of the ions. If the theory of Mutscheller is true the presence of gelatin in such solutions should change the boundary potential. Then measurements of the transference numbers of sulfuric acid by this method would determine whether gelatin affected the boundary potential.

Since gelatin precipitates the heavy metals, it was obvious that precipitation would result if it were added to a sulfuric acid solution saturated with mercurous sulfate. Since, however, the influence of the gelatin on transference numbers is due only to its effect on the boundary potential, it is unnecessary to introduce gelatin into the electrode containers.

The cells were prepared as described and the siphons connecting the hydrogen and sulfate electrodes were filled with 0.1 *M* and 0.01 *M* solutions of sulfuric acid which contained a definite concentration of gelatin. They were then placed in the reservoirs, with the ends immersed in solutions of the same concentrations as that which surrounded the electrodes. The measurements were made as before, but showed a gradual progressive change. It was discovered that this was due to the diffusion of the gelatin from the siphons into the reservoirs and then into the solution which surrounded the electrodes. This made it necessary to devise a method which would prevent the diffusion and at the same time introduce no new potentials. Several devices were tried in which use was made of glass wool, filter paper, glass capillaries, and cotton wicks, before the following satisfactory method was found.

Ordinary cotton lamp-wicks were carefully washed by boiling in acid

of the same concentration as used in the cells. After washing and drying they were kept in 0.1 *M* and 0.01 *M* sulfuric acid solutions. Cells were prepared and so filled that the solution rose in the inner tube to the level *L* indicated in Fig. III. Gelatin solution identical with that in the siphon *S* was filled in the reservoirs to the level *L*. A wick *W* previously saturated with acid solution containing no gelatin was hung over the side of the inner tube so that one end of it was immersed in the plain solution of the inner tube and the other in the gelatin solution in the reservoir. This arrangement effectively eliminated the diffusion, provided the solutions in the inner tube and in the reservoir were maintained at the same level. No new potentials were introduced by this arrangement. All of the measurements were made with cells prepared in this manner. Measurements were made with concentrations of gelatin over a range of 0.5 to 20.0%. The results of these measurements are contained in 18 tables of which Table I is a sample.

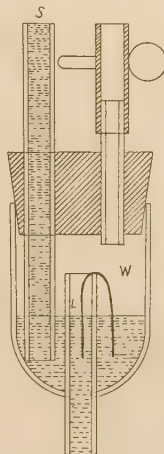


Fig. III—Detail of reservoir.

TABLE VI.—TYPICAL EXPERIMENTS.

Expt.	Date.	Time.	Bar.	E_{H^+}	E_{SO_4}	$E_{0.1}$	$E_{0.1}$	$E_{\text{H}^+} + E_{\text{SO}_4}$	$E_{0.01} - E_{0.1}$
			Mm.	Using 0.5% gelatin.					
1	1/14	12:30 A.M.	743.8			0.74189	0.80260		
2	1/24	9:30	748.4			0.74205	0.80264		
3	1/24	11:50	748.4			0.74203	0.80260		
Using 5% gelatin siphons introduced at 1 P.M.									
4	1/24	1:00 P.M.	747.8	0.01295	0.04750	0.74199	0.80235		
5	1/24	5:00	749.6	0.01290	0.04743	0.04210	0.80220	0.06033	0.06010
6	1/24	11:00	751.0	0.01292	0.04740	0.74217	0.80237	0.06032	0.06020
7	1/25	10:30 A.M.	754.2	0.01290	0.04779	0.74213	0.80260	0.06069	0.06047
Av.				0.01290	0.04754	0.74213	0.80239	0.06044	0.06026

The cell was set up on Jan. 23 at 2:30 P.M. The averages do not include the first four sets of readings.

In these tables the same arrangement of the data has been followed as in the previous tables. In order that a comparison of the values recorded in the separate tables may readily be made the average values in each table together with the transference numbers calculated therefrom have been summarized in Table VII.

The headings of Cols. 2, 3, 4, and 5 have the same significance as before. Cols. 6, 7, 8, and 9 contain the transference numbers calculated from the values in Cols. 2, 3, 4, and 5, as indicated in the head-

TABLE VII.—SUMMARY OF POTENTIALS AND TRANSPERANCE NUMBERS WITH GELATIN.

1. Table.	2. E_H	3. E_{SO_4}	4. $E_H + E_{SO_4}$	5. $E_{0.01} - E_{0.1}$	6. N_a $\frac{N_a}{E_H + E_{SO_4}}$	7. N_a $\frac{N_a}{E_{0.01} - E_{0.1}}$	8. N_c $\frac{N_c}{E_H + E_{SO_4}}$	9. N_c $\frac{N_c}{E_{0.01} - E_{0.1}}$	10. $N_a + N_c$ Cols 7 + 9.
Average without gelatin.	0.01131	0.04925	0.06056	0.06054 0.0%	0.1868	1.0808	0.8133	0.8135	1.0001
IX	0.01290	0.04754	0.06044	0.06026 0.5%	0.213	0.214	0.786	0.789	1.003
Av.	0.01289	0.04774	0.00063	0.06049	0.213	0.213	0.787	0.789	1.002
	0.01290	0.04764	0.06054	0.06037	0.213	0.214	0.787	0.789	1.003
XI	0.01480	0.04549	0.06029	0.06039 1.0%	0.246	0.245	0.754	0.753	0.998
XII	0.01507	0.04577	0.06084	0.06070	0.248	0.248	0.752	0.754	1.002
Av.	0.01494	0.04563	0.06056	0.06055	0.247	0.247	0.753	0.754	1.000
XIII	0.02476	0.03799	0.06275	0.06077 2.0%	0.395	0.407	0.605	0.625	1.033
XIV	0.02466	0.03699	0.06165	0.06067	0.400	0.407	0.600	0.610	1.010
Av.	0.02471	0.03749	0.06220	0.06072	0.397	0.407	0.603	0.617	1.025
XV	0.02708	0.03213	0.05921	0.06081 2.5%	0.457	0.445	0.543	0.528	0.974
XVI	0.02655	0.03239	0.05894	0.06064	0.450	0.438	0.550	0.534	0.972
Av.	0.02682	0.03266	0.05907	0.06072	0.453	0.442	0.547	0.531	0.973
XVII	0.03062	0.02809	0.05871	0.06086 3.0%	0.521	0.503	0.478	0.461	0.964
XVIII	0.03300	0.02839	0.06139	0.06065	0.537	0.544	0.462	0.467	1.011
Av.	0.03181	0.02824	0.06005	0.06075	0.529	0.524	0.470	0.464	0.987
XIX	0.03838	0.02278	0.06106	0.06058 5.0%	0.627	0.632	0.373	0.376	1.008
XX	0.03683	0.02539	0.06222	0.06039	0.592	0.607	0.408	0.419	1.026
Av.	0.03755	0.02408	0.06169	0.06069	0.610	0.620	0.390	0.398	1.017
XXI	0.03814	0.02406	0.06220	0.06098 10.0%	0.613	0.625	0.387	0.397	1.000
XXII	0.03655	0.02414	0.06069	0.06085	0.602	0.601	0.398	0.397	0.997
Av.	0.03735	0.02410	0.06145	0.06092	0.608	0.613	0.393	0.397	0.999
XXIII	0.04041	0.02267	0.06308	0.06085 15.0%	0.641	0.664	0.359	0.373	1.037
XXIV	0.04088	0.02219	0.06307	0.06076	0.648	0.673	0.352	0.305	1.038
Av.	0.04065	0.02243	0.06308	0.06081	0.645	0.669	0.356	0.369	1.038
XXV	0.04117	0.02057	0.06174	0.06074 20.0%	0.667	0.678	0.333	0.339	1.017
XXVI	0.04194	0.02078	0.06272	0.06071	0.669	0.691	0.331	0.342	1.033
Av.	0.04157	0.02068	0.06223	0.06073	0.668	0.685	0.332	0.341	1.025

ings. Col. 10 contains the sum of the N_a and N_c values of Cols. 7 and 9 and should always be equal to unity. The deviation from unity is an indication of the small error of the potentials used in their calculation. The accuracy with which the potentials of E_H and S_{SO_4} can be duplicated in the presence of gelatin, is shown by the closeness with which the averages for any two tables of the same concentration agree. From a comparison with similar values in the previous tables, it is plainly evident that when gelatin is present the agreement is less satisfactory than when it is not. This lack of agreement becomes greater the higher the concentration of gelatin. Table VIII is a summary of the averages of the potentials and transference numbers contained in Table VII.

TABLE VIII.—SUMMARY OF POTENTIALS AND TRANSFERENCE NUMBERS.

% Gel.	E_H .	E_{SO_4} .	N_a .	E_B .
0.0	0.01136	0.04918	0.187	0.02906
0.5	0.01290	0.04784	0.213	0.02746
1.0	0.01494	0.04563	0.247	0.02544
2.0	0.02741	0.03749	0.407	0.01676
2.5	0.02682	0.03266	0.442	0.01283
3.0	0.03181	0.02824	0.524	0.00822
5.0	0.03755	0.02408	0.620	0.00354
10.0	0.03735	0.02410	0.613	0.00362
15.0	0.04065	0.02243	0.668	0.00140
20.0	0.04155	0.02068	0.685	-0.00006

A consideration of the values recorded for N_a shows that they increase with increase in concentration of gelatin. The relation between the transference number of the anion and concentration of gelatin is shown by the curve in Fig. 4. In this curve the transference numbers are plotted as

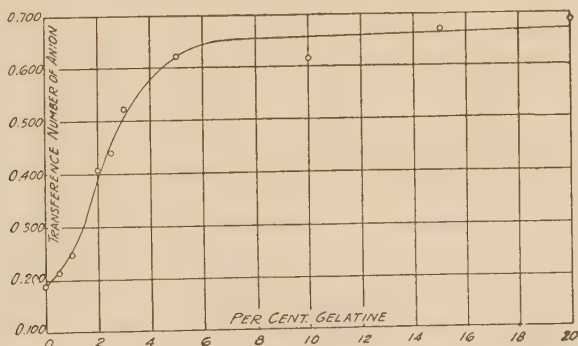


Fig. 4.— N_a -gelatin curve.

ordinates and the concentrations of gelatin as abscissas. The change in transference number with increase in gelatin is rapid at low gelatin concentrations, is gradual between 3 and 5%, and above this is not appreci-

able. If this represents an actual increase in the migration velocity of the anion, then there must be a corresponding decrease in the boundary potential (E_B). The values in the columns headed E_B and N_a indicate such changes. Since the boundary potential is opposed to the electrode potentials in the case of the hydrogen concentration cell (E_H) and is added to the electrode potentials in the case of the sulfate concentration cell (E_{SO_4}) a decrease in E_B would result in an increase in the value of E_H and a decrease in E_{SO_4} . That such changes do take place is indicated by the values in the columns headed E_H and E_{SO_4} .

It has been shown that the boundary potential depends on the transference numbers of the ions and the ratio of their concentrations in the two solutions. Therefore a change in E_B would result from a change in concentration or a change in transference number.

The value of E_B would be reduced by making the concentration of the solutions more nearly equal. When exactly equal E_B would be zero, and when the concentration of the 0.1 M solution became less than that of the 0.01 M , the direction would be reversed.

To determine whether or not concentration changes are produced by the gelatin, concentration cells of the type $Pt_H | 0.1 M H_2SO_4 | KCl | 0.1 M H_2SO_4 + \text{gel.} | Pt_H$ and $Pt_H | 0.01 M H_2SO_4 | KCl | 0.01 M H_2SO_4 + \text{gel.} | Pt_H$ were used. The data from these measurements are summarized in Table IX.

TABLE IX.

% Gel.	C_1 , 0.1 M .	E_x .	C_2 , 0.01 M .	E_z .
0	0.05946		0.012340	
1	0.05694	0.00070	0.007684	0.01216
2	0.05670	0.00122	0.002172	0.04458
3	0.05542	0.00181	0.000430	0.08609
4	0.05356	0.00268	0.000144	0.11418

It was impossible to work with concentrations of gelatin above 4% because of the excessive foaming of the solutions.

The first column contains the percentage of gelatin in the acid in one-half the cell. The columns E_x and E_z contain the measured potentials of the cells E_x and E_z when 0.1 M and 0.01 M solutions are used. In columns C_1 and C_2 are the hydrogen-ion concentrations in 0.1 M and 0.01 M solutions with gelatin, calculated by the use of the formula for concentration cells in which boundary potential has been eliminated. The results in columns C_1 and C_2 show that gelatin produces a relatively small decrease in the hydrogen-ion concentration of the 0.1 M solution, and a much greater relative decrease in the 0.01 M solution. The hydrogen-ion concentration of the 0.1 M solution is always greater than that of the 0.01 M ; therefore the reversal of the boundary potential (E_B) as shown in Table VIII cannot result from the concentration changes produced by the

gelatin. Since E_B can be decreased or reversed only by a change in concentration or transference number, the observed change must be due to a change in the transference number.

Since it has been shown above that the gelatin produces changes in the hydrogen-ion concentration, new potentials are developed at the boundaries between the solutions in the wicks and the gelatin solution in the reservoirs. The locations and directions of the boundary potentials, E_B , E_x and E_z together with E_H and E_{SO_4} are represented digrammatically in Fig. 5. The location of the boundary potentials is shown also by the same letters in Fig. 1. E_B represents the potential within the siphon, that is, the potential which has been considered thus far. E_x and E_z represents the potentials at the contact of the solutions in the reservoirs. E_H and E_{SO_4} are the measured potentials and are the algebraic sums of the potentials at the electrodes and the boundary potentials E_x , E_B , and E_z .

The potentials E_x , E_B , and E_z which result from the presence of the gelatin can be calculated from the data in Table IX by the use of the usual formula for boundary potential. These calculations were made and the results are included in Table X. The potentials at E_x and E_z are oppositely directed and the resultant potential is therefore their difference. These differences are recorded in the column headed $E_z - E_x$. The total potential at E_B is opposed to the resultant potentials $E_z - E_x$ and may be considered as the sum of the original boundary potential E_B (0.02906) and the potential resulting from the changes in concentration produced by the gelatin. Therefore the differences between the total potentials E'_B and the original potential E_B (0.02906) is that due to the changes in concentration produced by the gelatin. The values of these differences are recorded in the column headed $E'_B - 0.02906$. As the values in the column headed $E'_B - 0.02906$ are practically identical with those in $E_z - E_x$ and oppositely directed, their combined effect must be zero. This shows that the potentials E_x and E_z at the contacts between the solutions in the wicks and the gelatin solutions in the reservoirs are entirely compensated by the potential ($E'_B - 0.02906$) simultaneously developed at the boundary E_B . Therefore any boundary potential produced by the introduction of gelatin cannot result from changes in concentration. The experimental data, however, show that

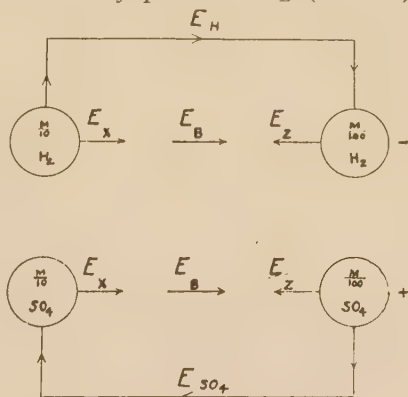


Fig. 5.—Diagram of potentials.

the boundary potential E_B is changed by the addition of gelatin. Since this cannot be due to concentration changes it must result from a change in the transference numbers of the hydrogen and sulfate ions or from an actual change in the kind of ions present. This may be effected in several ways; (1) by the removal of either ion as the result of its being selectively adsorbed by the gelatin; (2) by a change in the velocity of either ion; (3) by chemical reaction with the gelatin resulting in the formation of new ions.

TABLE X.—BOUNDARY POTENTIAL CALCULATIONS.

% Gel.	E_H	E_{So_4}	E_B	E_x	E_z	$E_z - E_x$	$E_B - 0.02906.E'_B$
1	0.01494	0.04563	0.02544	0.00077	0.00878	0.00801	0.00804
2	0.02941	0.03749	0.01676	0.00085	0.03215	0.03107	0.03124
3	0.03181	0.02824	0.00822	0.00132	0.06210	0.06078	0.06094
4				0.00196	0.0825	0.08054	0.08054

Since the conductivity of a solution is affected by any change in the number and the mobility of its ions, it was thought that conductivity measurements would furnish information as to the nature of the influence of the gelatin. Measurements were made of the conductivity of 0.1 *M* and 0.01 *M* sulfuric acid solutions which contained different concentrations of gelatin. The concentration of gelatin was varied from 0 to 20%. As it was necessary to apply a correction for the conductivity of the gelatin in conductivity water, a series of measurements was made with gelatin solutions over this same range of concentration. The corrected conductivity values are recorded in Table XI.

TABLE XI.—CONDUCTIVITY OF SULFURIC ACID SOLUTIONS IN PRESENCE OF GELATIN

% Gel.	0.1 <i>M</i> .	0.01 <i>M</i> .
0	0.037704	0.005011
1	0.033695	0.002413
2	0.030608	0.000948
3	0.027516	0.000755
4	0.02423	0.000686
10	0.009907	0.000462
15	0.003987	0.000349
20	0.002800	0.000233

The effect of the gelatin on the conductivity of the 0.1 *M* and 0.01 *M* sulfuric acid solutions is also shown by the curves in Figs. 6 and 7. The conductivities are plotted as ordinates and the concentrations of gelatin as abscissas. These curves show that the gelatin produces a greater relative change in the conductivity of the 0.01 *M* sulfuric acid solution than in the conductivity of the 0.1 *M* solution. It should be recalled that in the concentration-cell measurements, recorded in Table IX, the gelatin produced a much greater relative change in the hydrogen-ion concentration of the 0.01 *M* solution than in the 0.1 *M*. In fact, by the addition of about 3 to 4% of gelatin, the concentration of the 0.01 *M* solution was

reduced practically to zero. From Fig. 7 it is readily seen that by the addition of about 3% of gelatin the conductivity has been reduced almost to zero. This indicates that not only is the hydrogen-ion concentration reduced by the addition of gelatin but that sulfuric acid is removed as a whole.

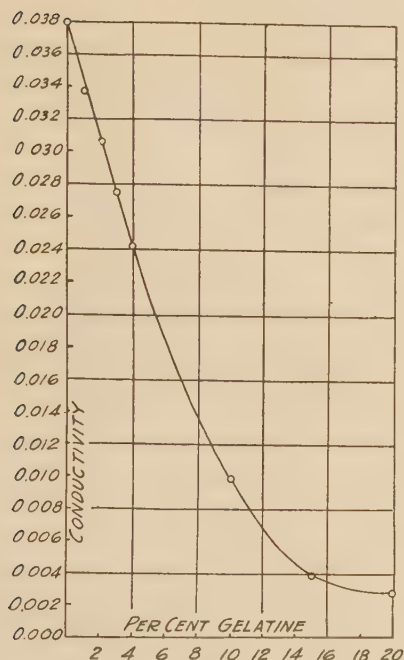


Fig. 6.—Conductivity-gelatin curve for 0.1 M H_2SO_4 .

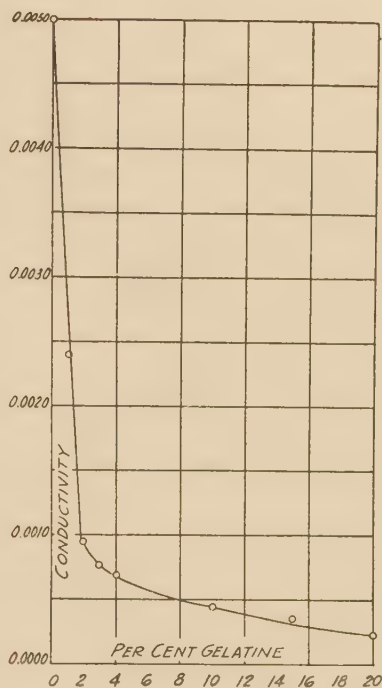


Fig. 7.—Conductivity-gelatin curve for 0.01 M H_2SO_4 .

Several calculations were made involving the conductivity data and potential data in an effort to determine whether the gelatin produced an actual change in the mobility of the ions, but it was impossible to conclude from these calculations whether the effects obtained were due to concentration changes alone or to concentration changes together with changes in mobility or the presence of new ions.

Two explanations have been offered to account for the action of gelatin, one of which assumes that the ions of the acid are "absorbed" by the gelatin, and the other that a highly dissociable chemical compound is formed. Supporters of the first theory are H. G. Bennett¹¹ and A. Mutscheller;¹⁰

¹¹ Bennett, *J. Am. Leather Chem. Assoc.*, **13**, 270 (1918).

and favoring the second theory are H. R. Procter,¹² H. R. Procter and J. A. Wilson,¹³ J. Loeb,¹⁴ and W. O. Fenn.¹⁵

It has been shown in this investigation that some of the properties of sulfuric acid are altered by the presence of gelatin. A summary of the data obtained in the work on its influence on the transference number of the anion of sulfuric acid is contained in Table VIII. It may be observed that the boundary potential (E_B) is reduced from +0.02906 to -0.00006. Corresponding to this decrease in boundary potential, there is an increase in the potential of the hydrogen concentration cell (E_H) from 0.01136 to 0.04155 and a decrease in the potential of the sulfate concentration cell (E_{SO_4}) from 0.04918 to 0.02068. There is an apparent increase in the transference number of the anion from 0.187 to 0.685. Any factor which would increase the numerical value of E_H and decrease E_{SO_4} would give the observed effect of a decrease in the boundary potential and an increase in the transference number of the anion. This factor was at first believed to be the result of changes in concentration which are recorded in Table IX, due to the presence of the gelatin. A careful consideration of the boundary potentials E_x , E_B , and E_z which result from these changes in concentration leads, to the conclusion that they should neutralize each other. The data in Table XI show this to be the fact. Therefore this effect was not due to the concentration changes brought about by the introduction of the gelatin. This led to the conclusion that the observed changes in the potentials of the concentrations cells resulted from a change in the boundary potentials. This decrease in the boundary potential could be produced by any one of three factors. An actual change in the transference numbers; a decrease in the concentration of the 0.1 *M* solution such that it was less than the 0.01 *M* solution; or by a change in the kind of ions present. Since the second of these factors is eliminated by the data recorded in Table IX, which shows that such concentration changes are impossible, it appears that the decrease in boundary potential must be due to the other factors.

As there is a possibility that a chemical compound which ionizes is formed, the facts are considered also from this point of view. If such is the case there should be a fairly close relation between the amount of gelatin added and the amount of acid removed. This would explain the decrease in hydrogen-ion concentration and decrease in conductivity observed. If such a reaction occurs new compounds are formed and some of the hydrogen ions are replaced by complex gelatin ions which results in the increase in the transference number of the anion as observed. No

¹² Procter, *J. Chem. Soc.*, **100**, 342-3 (1911); **105**, 313 (1914).

¹³ Procter and Wilson, *ibid.*, **109**, 307 (1916).

¹⁴ Loeb, *J. Gen. Physiol.* **1**, 39-60, 237-54 (1918); **2**, 363-85, 483-504, 559-80 (1919).

¹⁵ Fenn, *J. Biol. Chem.*, **33**, 279-94, 439-51 (1918); **34**, 141-60, 415-28 (1918).

data were obtained from which the exact amount of sulfuric acid removed by a definite weight of gelatin could be determined.

From the curve for the conductivity of the 0.1 *M* sulfuric acid solution, Fig. 6, it appears that the conductivity of the solution is reduced a definite amount for each additional per cent of gelatin. The addition of the first per cent of gelatin in the 0.01 *M* solution also produces about the same reduction in conductivity. This indicates that a definite quantity of gelatin removes a definite amount of sulfuric acid from the solutions. If the compound formed dissociates, and some evidence has been obtained from other sources that it does then the conductivity curves will tend to flatten at the higher concentrations of gelatin. Loeb¹⁴ has been led to believe that in acid solutions gelatin reacts to form gelatin salts of the acid and in the case of sulfuric acid he states that the gelatin sulfate formed has the composition represented by the formula $\text{gel}_4(\text{SO}_4)_2$. The dissociation of such a salt would result in the formation of a slowly moving complex colloidal gelatin cation and a sulfate anion. The transference number of the anion of such a compound would be greater than that of the cation. This conforms to the observed facts. Furthermore, such a compound would show some conductivity, so that for the higher concentrations of gelatin the decrease in conductivity would no longer be proportional to the gelatin added. This is borne out by the flattening of the conductivity curves at the higher concentrations of gelatin. It should be pointed out that the sharp bend in the conductivity curve of the 0.01 *M* solution, Fig. 7, occurs at about the same concentration as a similar bend in the gelatin transference-number curve, Fig. 4; furthermore it is shown from the gelatin concentration cells, Table IX, that the sulfuric acid in 0.01 *M* solution is practically all removed at this same concentration of gelatin.

These facts indicate that sulfuric acid as such is removed by the addition of gelatin to the solution. Accordingly the apparent change in transference numbers is due not to an actual change in the velocity of the H^+ and SO_4^{--} ions, but to the presence of new ions in the solution resulting from the dissociation of the gelatin-sulfate compound.

It is the opinion of the author that the action of gelatin and sulfuric acid results in the formation of a single dissociable product in which the H^+ ion of the acid loses its identity. It is further believed that in the presence of a base a similar product would result in which the identity of the OH^- ion would be lost and that in the presence of a neutral salt solution no similar action would result. At the present time investigations are being conducted by the author to confirm this hypothesis.

Summary.

1. A method has been described for the determination of the transference numbers of a uni-bivalent electrolyte by the measurement of the potentials of concentration cells.

2. The transference number of the anion of sulfuric acid for concentrations between 0.1 *M* and 0.01 *M* has been measured and found to be 0.1868 ± 7 at 25°.

3. It has been shown that dissociation values determined from freezing-point data are more satisfactory for calculating the potentials of concentration cells than those obtained from conductivity data.

4. A correction to the formula for the potential of a concentration cell has been developed which takes into account the undissociated part of the acid.

5. It has been shown that the concentration-cell method is entirely satisfactory for the determination of the transference numbers of sulfuric acid.

6. The effective concentration of 0.1 *M* and 0.01 *M* sulfuric acid solutions has been found to be reduced by the addition of gelatin.

7. The transference numbers of 0.1 *M* and 0.01 *M* sulfuric acid solutions have been found to be altered by the presence of gelatin.

8. The conductivities of sulfuric acid solutions have been found to be reduced by the presence of gelatin.

9. An hypothesis has been offered to account for the action of gelatin in the presence of electrolytes.

